STUDY OF Zn–Co ALLOY COATINGS MODIFIED BY NANO- TiO_2 PARTICLES INCORPORATION

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The purpose of this paper is to investigate the effect of TiO_2 nanoparticles contents on structural properties, microhardness and corrosion resistance of Zn-Co alloy coating and Zn-Co-TiO_2 composite coatings is electrodeposited on steel substrate in the acid sulfate bath, The smaller grain size of the composite coatings is observed in the presence of TiO_2 and it is confirmed by the images of scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The corrosion performance of coating in the 3 % NaCl as a corrosive solution is investigated by potentiodynamic polarization and electrochemical impedance spectroscopy EIS methods. It is found that the incorporation of nanoparticules in Zn–Co alloy coating have better corrosion resistance and the values of R_{ct} and Z_w increase, while the values of C_{dl} decrease with the increasing of nanoparticules.

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1. Introduction

Electroplated binary Zn-Malloys, where metals are an Fe group such as Fe, Co, Sn, Ni, Mn and Cr [1-3], exhibit improved properties compared to pure Zn is nowadays of great importance not only for corrosion protection of metallic substrates but also used in a variety of industrial applications, one of the first applications such as catalysts, electrodes for batteries, magnetic uses [4-6] and printing plates the most common examples are being Zn–Fe [7–8], Zn–Co [9-12] and Zn–Ni [13–16], It is believed that the composition and corrosion resistance of composite coatings are influenced by several interrelated parameters, such as chemical composition of the electrolyte, the concentration of metal ionssolution temperature and pH, agitation, type of applied current and current density [17].

Electrodeposited composites are obtained by adding insoluble solid particles to an electrolytic bath [18]. These insoluble particles can be oxides such as (Al_2O_3, TiO_2, ZrO_2, SiO_2, SiC).They are used as a second phase because theypossess good chemical stability, provide better mechanical properties, and good wear resistance and corrosion resistance at elevated temperature [13,18].Zn–Co composite coatings for example ZnCo–Al_2O_3 andZnCo–SiC [19],TiO_2have been used to improve different metallic and organic coatings. TiO_2 with a metalliccoating, significantly contributes to wear and corrosion resistance, better hardness [20-21].In their works, indicated (who) that the porous nanocomposite coatings exhibit higher corrosion resistance when compared to Zn–Co coatings and it is strongly affected by the TiO_2 structure and concentration, The composite coatings has been characterized, morphological (SEM), (XRD), and electrochemical properties of the composite coatings had been studied by potentiodynamic polarization and electrochemical impedance spectroscopy in a solution of 3 % NaCl.

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2. Experimental details

2.1. Coating preparation

Nanocomposite coatings Zn–Co, with different concentrations of nanoparticules of TiO_2, have been prepared on mild steel substrates form plates (25mm x 5mm x 2mm) which were used as cathode electrode, by electrodeposition technique. The zinc plates were used as anodic electrodes. The distance between the anode and the cathode is maintained at 2 cm to ensure deposit uniformity. Before deposition, the substrates were polished mechanically, degreased in alkaline solution, treated in HCl (10 %) solution, cleaned in acetone and then rinsed with distilled water. The process was carried in sulphate bath at current density of 30 mA cm^{-2} and temperature of 30°C during 30 minutes. The chemical composition of the basic electrolyte of Zn–Co alloys deposition is given in Table 1. Electrodeposits Zn–Co is obtained by varying the concentration of TiO_2 in the bath (5, 10, 20 $g{\cdot}l^{-1}$).

Table 1.Solution composition and conditions for alloy electroplating [9, 26].

Electrolyte I	Concentration ($g{\cdot}l^{-1}$)	Plating parameters
$ZnSO_4{\cdot}7H_2O$	57.5	30°C and pH=3,5 constant current densities at 30 mA cm^{-2} for 60s
$CoSO_4$	52.5	
H_3BO_3	9.3	
Na_2SO_4	56.8	
$Na_3C_6H_5O_7$	56.8	

2.2. Coating characterization

The phase structure of the coatings is determined using X-ray diffractionwith a D8 Advance-Brucker using a Cu Kα radiation (λ= 1.5406Å) and 2θ= 0.02° as a step.

Scherrer's formula is used for the determination of the coatings crystallite sizes from the X-ray peak broadening of the (101) diffraction peak at [9.27]:

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

where D is the grain size, λ is the X-ray wavelength, β is the corrected peak full width at half-maximum intensity (FWHM), and θ is Bragg angle position of the considered peak.

The deposits surface morphology was studied by scanning electron microscopy (A JEOL model JSM6390LV).

Microhardness of coatings is was measured using a load of 100 g with a holding time of 15s by using a Vickers hardness tester, andthe average of ten hardness measurements was quoted as the hardness value.

The corrosion behavior and the protection performance of Zn-Co alloy and Zn-Co- TiO2 composite coatings were studied by using electrochemical impedance spectroscopy (EIS) and electrochemical Tafel extrapolation (TE) in 3,5 % wt NaCl solution. The tests were performed using a potentiostatgalvanostat (a Volta Lab 40 model). A coated sample was served as a working electrode, the counter electrode was platinum with a surface of 1 cm2 and the Hg/HgO/ 1 M KOH is used as a reference electrode. The impedance data were obtained at open-circuit potential and the measurements were carried out over a frequency range of 100 kHz-10 MHz using the amplitude of sinusoidal voltage (10mV). Potentiodynamic polarization with a scan rate of 50mV/s was applied in order to study the anodic dissolution of the coatings. The corrosion current density (Icorr) and corrosion potential (Ecorr) were determined using TE.

3. Results and discussion

3.1. Phase structure

Fig. 1 shows XRD patterns for four Zn-Co alloy coating and Zn-Co-TiO2 composite coatings.The metallic phases are well crystalline and can be ascribed to the Zn hexagonal structure in Fig 1(a). Only the diffraction lines of zinc-rich (η-phase) (JCP: 4-0831 [19]) and cubic Co_5Zn_{21} phase (γ-phase) (JCPDS N: 22-0521). The presence of TiO2 diffraction lines in the X-ray spectra of the deposits Fig. (1 .d) confirmed also the formation of the Zn–Co-TiO2 composite layers. The analysis of diffractograms shows that the composition of the plating bath has a strong influence on the crystal orientation in the deposit. Thus, the diffraction maximum (101) of Zn-Co in the composite layers decreases,These results are in accordance with those stated in the literature, that the particles embedded in the coatings can affect the preferred orientation of the metallic matrix as a consequence of changes on the metal deposition mechanism [21].

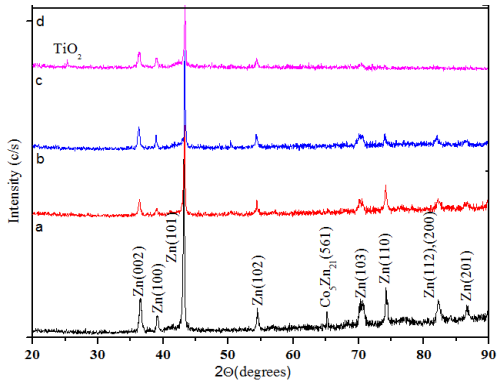

Fig. 1.XRD spectra of (a) Zn-Co alloy coatings and (b) Zn-Co-TiO_2 (5 g /l TiO_2), (c) Zn-Co-TiO_2 (10 g /l TiO_2) , (d) Zn-Co-TiO_2 (20 g /l TiO_2) Composite coatings.

Crystallite sizes were determined using the Scherer formula. For all coatings, the profile of (101) peak exhibits Lorentzian line shape, like shown as it is showed in Table 2.

Table 2.Values of the crystallite size obtained from the strongest diffraction line of the metallic phases.

Electrolyte	hkl	2θ(°)	Crystal size (nm)
Zn-Co (0 g /l TiO_2)	(101)	43.15	55.99
Zn-Co-TiO_2 (5 g /l TiO_2)	(101)	43.18	43.08
Zn-Co-TiO_2 (10 g /l TiO_2)	(101)	43.28	39.05
Zn-Co-TiO_2 (20 g /l TiO_2)	(101)	43.39	30.77

The grain sizes significantly decrease from 55.99nm to 43.08 nm with increasing TiO_2 nanoparticles concentration from zero to 5g/l in the electrolyte, and slowly decreases for a concentration more than 10 g/l,20 g/l (Table 2), indicates that the composite coatings have smaller grain size than alloy coatings. Therefore, incorporation of TiO_2 nanoparticles in the coating refined the crystals. It is worth noting that all coatings grain sizes are in the nanometer scale, confirming the nanocrystalline structure of Zn-Co and Zn-Co-TiO_2composite coatings.This finer structure may be at the origin of the decrease in the whole peaks intensity of the coated steel substrates and may be at the origin of the higher hardness of this deposit as mentioned previously [22,23].

3.2. Surfacemorphology

The morphology of these coatings plated in different compositions and for two magnifications 20 and 30μm is presented in fig. 2(a-d). it is clearly shown that in general, the surface of the Zn-Co alloy coating (fig. 2 a) is uniform, homogenous and consists of irregular crystals particles with a clear grey color [9], the grain size of the Zn-Co-TiO_2 composite coating (fig. 2 a, b, and d) sample is smaller and more uniform crystals when compared with the Zn-Co coating. asit is seen in fig. 2 b.The incorporation of TiO_2 nanoparticles, with feeble amount, in the Zn-Co coating retards the crystal growth and leads to a smaller grain size [24]. whereas for Zn-Co-TiO_2(10 g /l TiO_2), the grains become greater having rocky-like shape as seen in fig. 3c (not the same magnification 30 μm) then they become separated rocky-like shape (see fig. 3d) for the lest concentration of TiO_2 (10g/l).

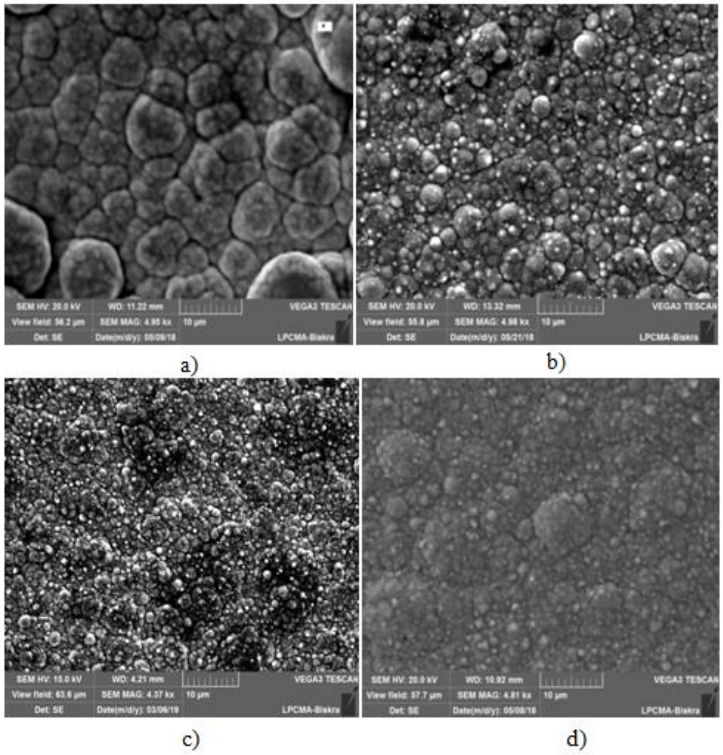

Fig. 2.Surface morphology of (a) Zn-Co alloy coatings and (b) Zn-Co-TiO_2 (5 g /l TiO_2), (c) Zn-Co-TiO_2 (10 g / L TiO_2) , (d) Zn-Co-TiO_2 (20 g /l TiO_2) Composite coatings.

3.3. EDX analysis of the Zn-Co-TiO_2composite coating

For further analysis of alloy coatings nanoparticles EDAX analysisis used, Fig. 3 (a-c) for Zn-Co-TiO_2 (5, 10, and 20 g /l TiO_2)confirms the presence of TiO2 in those alloys. This analysis showed also a doublet signal peak for TiO_2at 0.5 and approximately 5.5keV.

Chemical compositions of Zn-Co-TiO_2 composite coatings depend on the concentration of TiO_2, as shown in Fig 3. Also EDAX analysis shows that the Co content increases from 22% to 27% with increasing TiO_2 concentration in bath. The study of the impact of the TiO_2 nanoparticles in nucleation and growth of the Zn-Co films is in progress[22,25].

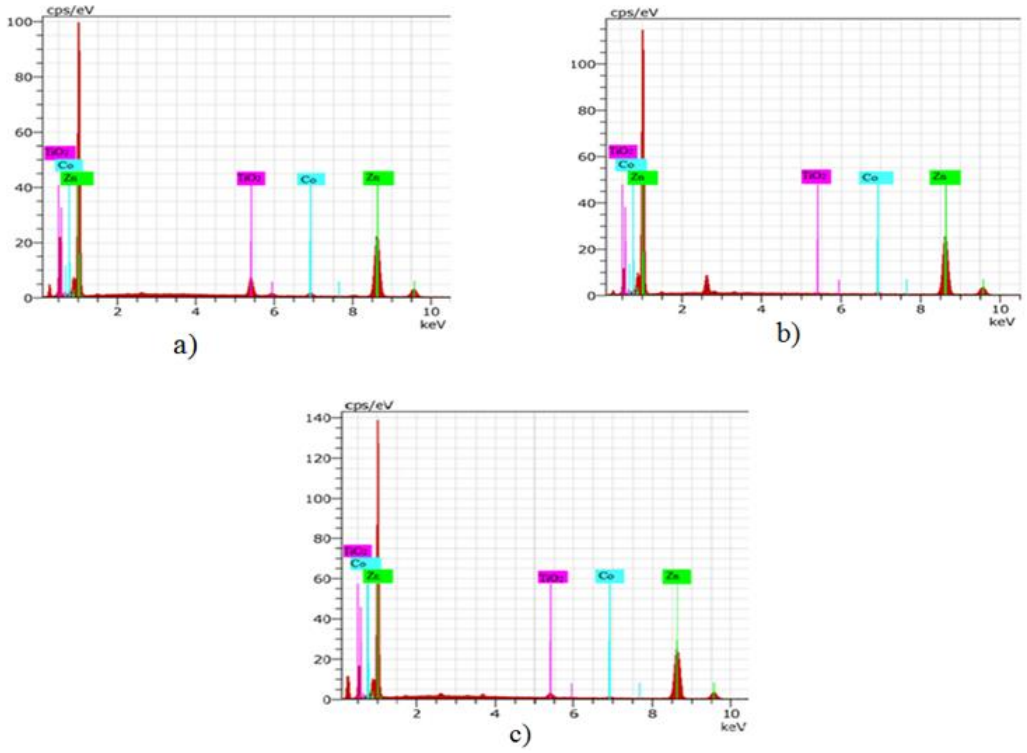

Fig. 3.EDAX of a) Zn-Co-TiO_2 (5 g /l TiO_2), (b) Zn-Co-TiO_2 (10 g / L TiO_2) , (c) Zn-Co-TiO_2 (20 g /l TiO_2) Composite coatings.

3.4. Micro hardness measurements

The microhardness results of Zn-Co alloy and Zn-Co-TiO_2 composite coatings electroplated at different agitation speeds are summarized in Table 2. The results indicated that Zn-Co- TiO_2 composite coatings showed higher microhardness compared to Zn-Co alloy coatings. The variation of microhardness results can be attributed to the incorporation of TiO_2 nanoparticles. The upper hardness of the coating is because of the deposit formation with fine-grainedstructure. As explanation to this hardness is that during its measurements, the easy movement of dislocationshas been obstructed by the dispersed particles in the fine-grained matrix which is shown in the case of composite coated samples. The hardness of nanocomposite coating depends directly on the TiO_2 content of nanocomposite coating[20,22,25].

Table 3.Values of micro-hardness Vickers hardness (HV) registered different electro deposition.

Coating	hardness
Zn-Co	177.8
Zn-Co-TiO_2 (5 g /l)	212
Zn-Co-TiO_2 (10 g /l)	250
Zn-Co-TiO_2 (20 g /l)	283

3.5. Potentiodynamic polarization studies

Tafel tests have been performed on Zn-Co alloy and Zn-Co-TiO_2 composite coatings in 3.5 % NaCl solution. Tafel polarization readings have been shown in Fig 4. The corresponding electrochemical parameters extracted from Tafel plots are summarized in Table 3. Results indicated that the corrosion potentials of Zn-Co-TiO2 composite coatings shift to the positive direction and corrosion current density decreased significantly compared to Zn-Co alloy coatings.TheZn-Co-TiO_2nanocomposite coatings have lower chemical activity than the Zn-Co

alloy coating and hence possess better chemical stability in the external environment. The better electrochemical performance of the Zn-Co-TiO_2nanocomposite coatings may be attributed to the reduction in the defect size of the nanocomposite coatings by the incorporation of nanoparticulates, which is helpful to diminish the surface in contact with the corrosive environmentalso help to prevent the corrosive pits from growing up, and the incorporation of nano-particulates contributes to accelerate the passivation process of the metal matrix as well. Subsequently, the corrosion resistance of the nanocomposite coatings wasimproved [20,22-25].

Table 4.Electrochemicalparameters of the coatings derived from Tafel plots.

Coating	E_{corr}	i_{corr}	B_a	B_c	R_p
Zn-Co	-430,4	2,9868	59,1	-36,1	4,25
Zn-Co- TiO_2 (5 g /l)	-401,7	1,3819	80,9	-87,3	8,61
Zn-Co- TiO_2 (10 g /l)	-389,6	0,9141	51,3	-48,4	11,64
Zn-Co- TiO_2 (20 g /l)	-349,1	0,6814	40,3	-79	15,86

3.6. Electrochemical impedance spectroscopy

EIS is a useful technique for ranking coatings [1, 9]. Fig. 5 shows the EIS Nyquist plots of the three alloys in 3,5% NaCl solution, where Z′ (ω) and Z″(ω) are the real and imaginary parts of the measured impedance, respectively, and ω is the angular frequency. The significantly higher impedance and larger diameter of the (incomplete) semicircle in the spectra of the ternary alloy reflect its high corrosion resistance, which can be related to a change in the film (coating) capacitance C_f, and not only control by the charge transfer resistance R_{ct}. The capacitive impedance at high frequencies is well related to the thickness and to the dielectric constant of the coating. From the data obtained in Table 4, one can conclude that the values of R_{ct} and Zw increase, while the values of C_{dl} decrease with the increasing of TiO_2nano-particles content, and this behavior is in good agreement with that obtained for the Tafel plot measurements,The spectra presented shows at least two time constants. The first time constant, recorded at higher frequency, is displayed as a depressed incomplete semicircle. The electrical-equivalent-circuit (EEC) parameters, describing the process included in this time constant are R_{ct} and C_{dl} [13]. The second time constant, depicted at lower frequencies, corresponds to a straight line Figs 6 .This linear dependence between the imaginary and real part of the capacitance is related to the diffusion process of the soluble species, while is called Warburg impedance (Z_w) Therefore, EEC parameters describing the process included in the second time constant clearly indicates the diffusion control of the soluble species. From the electrode surface to the bulk of solution [20]. Zn-Co-TiO_2 provides better protection against corrosion on the steel substrate [13]

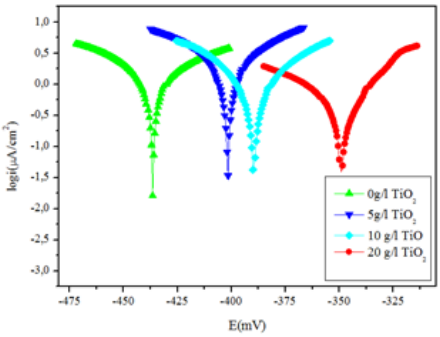

Fig. 4.Polarizing curves obtained for the alloy coatings in a 3.5 % NaCl solution at different concentrations of TiO2 nanoparticules.

Table 5.Simulation parameters obtained at the abandonment potential.

Coatings	R_e [Ω.cm^2]	R_{ct} [Ω.cm^2]	C_{dl} [F.cm^2]	Z_w [Ω.cm^2]
Zn-Co	6.579	0.934	0.159	1.253
Zn-Co- TiO_2 (5 g /l)	6.058	0.991	0.123	3.752
Zn-Co- TiO_2 (10 g /l)	7.017	1.275	0.027	4.128
Zn-Co- TiO_2 (20 g /l)	8.417	2.322	0.019	5.546

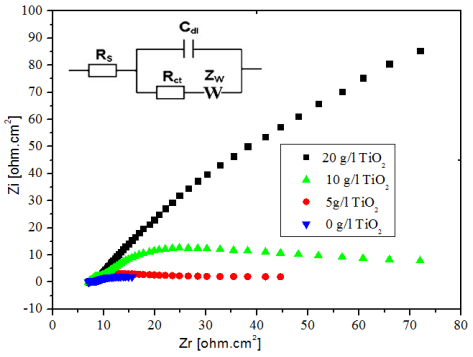

Fig. 5.Impedance diagrams for Zn-Co alloy and Zn-Co-TiO_2 composite coatings samples in 3% NaCl solution.

4. Conclusions

In this study, the effect of TiO_2 nanoparticles contents, in bath, on structural proporties, microhardness and corrosion resistance of Zn-Co alloy coating have beeninvestigated. The coatings have beendeposited on mild steel substrates by electrodeposition from a sulfate bath. Results from this investigation can be drawnby the following points:

XRD and SEM results indicate that Zn-Co alloy coationgZn-Co-TiO_2composite coatingform a mixture of two phases, zinc and cubic Co_5Zn_{21} phases, with smaller crystallite size,

The deposited coating with 20 g/l TiO_2 showed the maximum value of hardness 283HV, because of the increase of TiO_2nano-particulesconcentration in the plating bath.

Polarization resistances of Zn-Co composite coating increased with the increasing of theTiO_2nano-particules content.

The data obtained from electrochemical impedance spectroscopy (EIS) assumes that, the charge transfer resistance (R_{ct}) is higher and the capacity of the double layer (C_{dl}) value is lower for Zn-Co-TiO_2 composite coating containing 20 g /l TiO_2 alloy compared with those of Zn-Co matrix. This behavior is in good agreement with that obtained from Tafel plot measurements.

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References

[1] M. Diafi, N. Belhamra , B. T. Hachemi, B. Gasmi, S. Benramache , Acta Metallurgica Slovaca **21**, 226 (2015).

[2] A. Conde, M. A. Arenas, J. J. de Damborenea, Corrosion Science **53**, 1489 (2011).
[3] S. Ghaziof, W. Gao, Applied Surface Science **311**, 635 (2014).
[4] S. Fashu, C. D. Gu, J. L. Zhang,H. Zheng, X. L. Wang, J. P. Tu, Journal of Materials Engineering and Performance **24**, 434 (2015).
[5] G. D. Wilcox,D.R. Gabe, Corrosion Science **35**, 1251 (1993).
[6] N. Boshkov, K. Petrov, S. Vitkova, and G. Raichevsky , Surface & Coatings Technology **194**, 276–282 (2005) .
[7] A.B. Velichenko, J. Portillo, X. Alcobe, M. Sarret, C. Muller , Electrochimica Acta **46**, 407–414 (**2000)**.
[8] G.D. Wilcox, R.D. Gabe, Corrosion Science **35**, 1251- 1258 (**1993)**.
[9] M. Diafi ; L. Tahraoui ; K. Digheche ; F. Khamouli , Acta Metallurgica Slovaca **24**, 241-250 (**2018)** .
[10] K. Higashi, H. Fukushima, T. Urokawa, T. Adanya, K. Matsudo, Journal of Electrochemical Socience **128**, 2081 (1981).
[11] E. Gomez, E. Valles, Journal of Electroanalytical Chemistry **421**, 157 (1997).
[12] R. Fratesi, G. Roventi, G. Giuliani, C.R. Tomachuk, Journal of Applied Electrochemistry **27**, 1088 (1997).
[13] M. Diafi , S. Benramache , E. G. Temam , M. L. Adaika ,B. Gasmi , Acta Metallurgica Slovaca **22 ,** 171(**2016)**.
[14] L. Felloni , R. Fratesi , E. Quadrini , G. Roventi , Journal of Applied. Electrochemistry **22**, 657(**1992)** .
[15] G. Barcelo, J. Garci, M. Sarret, C. Muller, J. Pregonas, Journal of Applied Electrochemistry **24**, 1249 (1994).
[16] M. Mouanga, L. Ricq, P. Berçot, Surface and Coatings Technology**202**, 1645 (2008).
[17] S. Ghaziof, P. A. Kilmartin, W.Gao, Journal of Electroanalytical Chemistry **755**, 63 (2015).
[18] S. Pouladi, M.H. Shariat, M. E. Bahrololoom, Surface and Coatings Technology **213**, 33(2012).
[19] P. C. Tulio, I.A.Carlos, J. Appl.Electrochem. **39**, 1305 (2009).
[20] N. Belhamra, A. R. Boulebtina, K. Belassadi, A. Chala, M. Diafi, Diffusion Foundations **18**, 19 (2018).
[21] A. Vlasa, S. Varsara, A. Pop, C. Bulea, L. M. Muresan, J. Appl. Electrochem.**40**, 1519 (2010).
[22] A. Gomes, I. Almeida, T. Frade, A.C. Tavares, Materials Science Forum **636**, 1079 (2010).
[23] B.M. Praveen, T.V. Venkatesha, Applied Surface Science **254**, 2418 (2008).
[24] B. M. Praveen, T. V. Venkatesha, International Journal of Electrochemistry **2011**, 1 (2011).
[25] D. Blejan, D. Bogdana, M. Pop, A. V. Pop, L. M. Muresan , optoelectronics and advanced materials 5, 25 (**2011)** .
[26] M. Diafi, K. Degheche, H. Ben Temam, Journal of Fundamental and Applied Sciences **9**, 89 (2017).
[27] M. Diafi, M. Omari, Boletín de la Sociedad Española de Cerámica y Vidrio **51**, 337 (2012).